

HYDROGEN STORAGE METAL ALLOY,
METHOD FOR ABSORPTION AND RELEASE OF HYDROGEN
USING THE SAID ALLOY AND HYDROGEN FUEL BATTERY
5 USING THE SAID METHOD

TECHNICAL FIELD

10 The present invention relates to a method for
absorption and release of hydrogen where a hydrogen storage
metal alloy is repeatedly subjected to pressurization and
depressurization of hydrogen. In more detail, the present
invention relates to a hydrogen storage metal alloy having
15 a two-stage plateau- or inclined plateau-property.
Particularly, the present invention relates to a method
for absorption and release of hydrogen where the amount of
released hydrogen increases within practical pressure
ranges and temperature ranges, to a hydrogen storage metal
20 alloy suitable for such a method for absorption and release
of hydrogen and to a hydrogen fuel battery using the above
method for absorption and release of hydrogen.

25 RELATED ART OF THE INVENTION

At present, there have been worried not only about
acid rain due to an increasing NO_x (nitrogen oxides) but
also about the global warming due to an increasing CO₂ in
30 association with an increase in consumption of fossil fuel
such as petroleum and such environmental destruction has
become a serious problem. Therefore, our attention has
been greatly concentrated on development and practical
application of various kinds of clean energy which is
35 friendly to the earth. Part of means for developing such
a new energy is a practical application of hydrogen energy.
Hydrogen is a constituent element of water inexhaustibly

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present on the earth and can be not only produced using various kinds of primary energy but also utilized as fluid energy in place of conventionally used petroleum without the risk of destroying the environment because its product
5 by combustion is only water. In addition, unlike electricity, it has excellent characteristics such as its relatively easy storage.

10 In recent years, therefore, investigation has been actively conducted involving hydrogen storage metal alloys as media for storing and transporting hydrogen and their practical application has been expected. Such hydrogen storage metal alloys are metals/alloys which can absorb and release the hydrogen under an appropriate condition and,
15 by the use of such alloys, it is possible to store the hydrogen not only at lower pressure but also at higher density as compared to the case of the conventional hydrogen cylinders. In addition, the hydrogen volume density thereof is nearly equal to or rather greater than that of liquid or solid
20 hydrogen.

These hydrogen storage metal alloys which have been chiefly investigated are, for example, those alloys which each have a body-centered cubic (hereinafter, referred to
25 as "BCC") structure, including V, Nb, Ta or Cr-Ti-Mn alloys, Cr-Ti-V alloys, etc. as proposed in Japanese Unexamined Patent Publication (Kokai) No. 10-110225 (JP, A, 10-110225). It has been known that those alloys adsorb and store hydrogen in greater quantities as compared with AB₂ alloys such as
30 LaNi₅ and AB₂ alloys such as TiMn₂ which have been practically used until now. This is because the number of hydrogen absorbing sites in the crystal lattice is great in the BCC structure and the hydrogen absorbing capacity is as large as $H/M = \text{ca. } 2$ wherein H is occluded hydrogen
35 and M is a constituent element for the alloy (about 4.0 wt% in alloys of V, etc. having an atomic weight of around 50), being extremely large.

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It has been known that such a BCC alloy having a relatively large hydrogen absorbing capacity conducts a two-step reaction during the course of its absorbing hydrogen to form a hydride, as shown in Reilly and R. H. Wiswall, Inorg. Chem., 9 (1970), 1678). For example, V reacts with hydrogen at ambient temperature and forms two kinds of hydrides depending upon the pressure of hydrogen. At first, at the initial reaction stage wherein hydrogen pressure is low, a very stable hydride is formed as $V \rightarrow VH_{0.8}$ (α phase $\rightarrow \beta$ phase) (hereinafter, referred to as "low-pressure plateau part") and, at around room temperature, a reverse reaction thereof rarely happens. When further more hydrogen pressure is applied, a hydride is formed as $VH_{0.8} \rightarrow VH_{2.01}$ (β phase $\rightarrow \gamma$ phase; referred to as "high-pressure plateau part"). The equilibrium hydrogen pressure of this reaction is appropriate (approximately a few atmospheric pressure at around room temperature). Therefore, such V-containing BCC alloys have been briskly studied as high-capacity hydrogen storage metal alloys.

FIG. 1 is a conceptional chart of a PCT curve of a single substance V having a two-stage plateau comprised of the aforementioned low-plateau and high-plateau parts. The flat region at the hydrogen pressure of 10^{-1} Pa in FIG. 1 is a low-pressure plateau part and the flat region at the hydrogen pressure of 10^6 Pa is a high-pressure plateau part. The inclined region between the low-pressure plateau part and the high-pressure plateau part is a region complying with Sieverts's law. Besides V, an example of the metal having such a two-stage plateau is Nb (low-pressure phase: NbH , high-pressure phase: NbH_2). In addition, Ti shows a two-stage plateau by a transformation of $\alpha \rightarrow \beta \rightarrow \gamma$ although it operates at elevated temperature. An intermetallic compound having a two-stage plateau includes FeTi which works at near $40^\circ C$. Further, alloys such as (Zr,

Ti)V₂ show an inclined plateau and those alloys are also used as hydrogen storage metal alloys.

5 Examples of the prior art techniques presumably based upon the idea of developing a high-capacity hydrogen storage metal alloy relying on the above-mentioned two-stage plateau and inclined plateau characteristics are as follows:

10 (a) spinodal decomposition tissues are expressed in a body-centered cubic structure Ti alloy (the above JP, A, 10-110225);

(b) a Ti-Cr-V alloy is admixed with Cu and/or rareearth elements (the above JP, B2, 4-77061);

15 (c) a Ti alloy melt is rapidly cooled to form a BCC mono phase at room temperature (Japanese Unexamined Patent Publication (Kokai) No. 10-158755 (JP, A, 10-158755)); and

20 (d) a BCC alloy comprised as main elements of Ti-Cr is adjusted for its lattice constant (Japanese Unexamined Patent Publication (Kokai) No. 07-252560 (JP, A, 07-252560)).

25 Among the above-mentioned methods for absorbing and releasing hydrogen, those where temperature for absorption and desorption of hydrogen is mentioned are JP, A, 10-110225 and JP, A, 07-252560, both which disclose the methods where hydrogen is absorbed and released at a constant temperature, provided that, in the latter JP, A, 07-252560, the activating pretreatment is carried out by means of a
30 two-stage treatment comprising a low temperature in the former stage and a high temperature in the latter stage while the temperature for hydrogen absorption and desorption is constant (20 °C). In Japanese Patent Publication No. 59/38293 (JP, B2, 59/38293), hydrogen is absorbed with a
35 hexagonal Ti-Cr-V type alloy which is not a BCC alloy and a method of heating at 100 °C or higher (lines 32 to 39, column 4) is for absorbing and releasing hydrogen at a constant

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temperature as well.

5 However, in the hydrogen storage metal alloy having
the above-mentioned two-stage plateau characteristic such
as V-containing BCC alloy which has been often investigated
10 as the high-capacity hydrogen storage metal alloy, the
hydrogen-absorbing reaction at the low-pressure plateau
region proceeds only to the side of the reaction with
hydrogen at room temperature. Therefore, it has not been
15 carried out in the prior art that the hydrogen occluded is
taken out in such a low-pressure plateau region and used
as an effective hydrogen.

20 Thus, in the above-mentioned JP, A, 10-110225 and
JP, B2, 4-77061, such a low-pressure plateau region is not
referred to. In the latter patent, since there is a teaching
that the production of TiH_2 (high-pressure plateau region
compound) is to be avoided, only the hydrogen-absorbing
reaction between the low-pressure plateau region and the
high-pressure plateau region is utilized.

25 It is said that, in general, the amount of hydrogen
taken out from a body-centered cubic structure type hydrogen
storage metal alloy such as pure V and pure Nb is very low
as compared with the theoretical amount (Hydrogen Storage
Metal Alloy - Physical Properties and Applications, New
Edition, by Yasuaki Osumi, published by Agne Technique
Center, Japan, first printing of the new edition issued on
February 5, 1992, pages 340-341).

30 In AB₂ alloys such as LaNi₅ or BCC alloys, which
have been practically utilized up to now, it is possible
to control the equilibrium pressure regarding reaction with
hydrogen by controlling the alloy components. It is also
possible that the equilibrium pressure of the hydrogen
storage metal alloy with hydrogen is controlled by the
35 operating temperature. However, the conventional
research on alloys as such is not particularly based on
consciousness of improvement in the hydrogen-absorbing

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characteristic at the above-mentioned low-pressure plateau region.

Accordingly, it is believed that, in order to
5 increase the hydrogen absorption capacity in the
aforementioned BCC type hydrogen storage metal alloy, it
is effective that the hydrogen in the reaction of α phase
 $\rightarrow \beta$ phase, i.e., the reaction at the low-pressure plateau
part (for example, the reaction of $V \rightarrow VH_{0.8}$ in the case
10 of V), contributes to the reaction of absorption and
desorption in addition to the β -phase region of the BCC
type alloy (a portion complying with a Sieverts's law between
a low-pressure plateau region and a high-pressure plateau
region). However, such a means has not been disclosed yet.

Accordingly, an object of the present invention
is, with regard to the conventional pure V or pure Nb showing
a two-stage plateau or inclined plateau region or BCC solid
solution alloys including not only solid solutions showing
20 a hydrogen absorption/desorption reaction similar to the
above-mentioned metal, but also Ti-Cr system alloys, etc.,
to provide a hydrogen storage metal alloy in which the
hydrogen not only between α phase $\rightarrow \beta$ phase, i.e. in
the reaction at the low-pressure plateau region but also
25 at a low-pressure β phase region (a low-pressure region
showing a behavior similar to a Sieverts's law between a
low-pressure plateau region and a high-pressure plateau
region) is made contributed in an absorption/desorption
reaction of hydrogen in a reversible manner so that much
30 more amounts of hydrogen can be absorbed and released and
also to provide not only a method for absorbing and releasing
hydrogen with the said alloy but also a hydrogen fuel battery
using the said method.

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SUMMARY OF THE INVENTION

In order to achieve the aforementioned objects, the present invention provides a novel hydrogen storage metal alloy. According to the present invention, the novel hydrogen storage metal alloy has the following characteristics:

(1) it has as its main phase a body-centered cubic structure-type phase exerting a two-stage or inclined plateau characteristic in a hydrogen storage amount vs hydrogen pressure relation, and

(2) the composition ratio of constituent metals for the alloy is adjusted to an appropriate range in order to reduce the stability of the hydrogen occluded in the alloy during the low-pressure plateau region or the lower plateau region of the inclined plateau such that an alloy temperature (T_2) during at least a period in a hydrogen release process can be brought to higher than an alloy temperature (T_1) in a hydrogen-absorption process ($T_2 > T_1$) whereby at least part of the occluded hydrogen will be made desorbable during the low-pressure plateau region in the above-mentioned two-stage plateau or the lower plateau region of the inclined plateau.

Such characteristics lead to the following:

the occluded hydrogen can be unstabilized in the alloy so that the alloy temperature may be brought to high (T_2) during the hydrogen desorption process, thereby facilitating the release of hydrogen during the aforementioned low-pressure plateau region or the lower plateau region of the inclined plateau region, and therefore the occluded hydrogen at the low-pressure plateau region or the lower plateau region of the inclined plateau region, which has been neither desorbed nor utilized at all, can be taken out as utilizable hydrogen, with the result that the amount of the utilizable hydrogen in such a hydrogen storage metal alloy will be increased.

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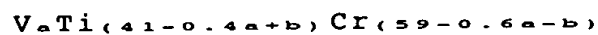
It is preferred that the hydrogen storage metal alloys of the present invention are those wherein the alloy temperature (T1) during the hydrogen-absorbing process may range from the extremely low temperature in the living areas on the earth to 373K.

As a result thereof, the alloy temperature (T1) during the hydrogen-absorbing process can be made near an ambient temperature region whereby the practicability can be improved.

It is preferred that the hydrogen storage metal alloys of the present invention are V alloys which each not only have a suitably adjusted composition to reduce the stability of the occluded hydrogen as aforementioned but also contain 0 to 95 at% of at least one or more members selected from the group consisting of Nb, Ta, W, Mo, Ti, Cr, Mn, Fe, Al, B, Co, Cu, Ge, Ni and Si.

As a result thereof, the alloys each having such a composition are highly effective in unstabilizing the occluded hydrogen therein and therefore suitable for releasing a large amount of hydrogen therefrom during the low-pressure plateau region or the lower plateau region of the inclined plateau by raising the alloy temperature during a hydrogen-desorbing process.

It is preferred that the hydrogen storage metal alloys of the present invention are those alloys which each have not only a suitably adjusted composition to reduce the stability of the occluded hydrogen as aforementioned but also a fundamental composition of the formula:



wherein $0 \leq a \leq 70$ at% and $-10 \leq b \leq 10$ at%.

As a result thereof, the alloys each having such a composition can occlude a large amount of hydrogen at the

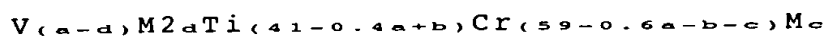
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high-pressure plateau region and are greatly effective in unstabilizing the occluded hydrogen therein. Therefore, such alloys are preferable to release a large quantity of occluded hydrogen during the low-pressure plateau region or the lower plateau region of the inclined plateau by raising the alloy temperature during the hydrogen-desorbing process and have an effective amount of utilizable hydrogen in great quantities, thereby giving a high practicability.

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It is preferred that the hydrogen storage metal alloys of the present invention are those alloys which each have not only a suitably adjusted composition to reduce the stability of the occluded hydrogen as aforementioned but also a fundamental composition of the formula:

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wherein $0 \leq a \leq 70$ at%, $-10 \leq b \leq 10 + c$, $0 \leq c$, $0 \leq d \leq a$, M is at least one or more members selected from the group consisting of Nb, Mo, Ta, W, Mn, Fe, Al, B, C, Co, Cu, Ge, Ln (various lanthanoid metals), N, Ni, P and Si, and M₂ is at least one or more members selected from the group consisting of Mo, Nb, Ta, W, Mn, Fe and Al.

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As a result thereof, the alloys each having such a composition can occlude a large amount of hydrogen at the high-pressure plateau region and are greatly effective in unstabilizing the occluded hydrogen therein. Therefore, such alloys are preferable to release a large quantity of occluded hydrogen during the low-pressure plateau region or the lower plateau region of the inclined plateau by raising the alloy temperature during the hydrogen-desorbing process and have an effective amount of utilizable hydrogen in great quantities, thereby giving a high practicability. In addition, as a result of suitable admixture with at least one or more elements selected from

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process ($T_2 > T_1$).

Such characteristics lead to the following: it is now possible to take out as a utilizable hydrogen the occluded hydrogen at the low-pressure plateau region or the lower plateau region of the inclined plateau which has not been desorbed and utilized at all whereby the amount of utilizable hydrogen can be increased in the hydrogen storage metal alloy.

It is preferred that the alloy temperature (T_1) during the above hydrogen-absorbing process is within a range of from the extremely low temperature in the living areas on the earth to 373K in the method for absorbing and releasing hydrogen by using the hydrogen storage metal alloy according to the present invention.

As a result thereof, the alloy temperature (T_1) during the hydrogen-absorbing process can be made near an ambient temperature region whereby the practicability can be improved.

It is preferred that the method for absorbing and releasing hydrogen according to the present invention comprises using a hydrogen storage metal alloy wherein the composition ratio of the constituent metals for the alloy is adjusted to an appropriate range in order to reduce the stability of the hydrogen occluded in the alloy during either the low-pressure plateau region or the lower plateau region of the inclined plateau such that the temperature of the said alloy can be brought to the above high temperature (T_2) whereby at least part of the occluded hydrogen will be made desorbable during either the low-pressure plateau region in the above-mentioned two-stage plateau or the lower plateau region of the inclined plateau.

As a result thereof, the occluded hydrogen can be unstabilized in the alloy, thereby facilitating the release of hydrogen from either the above low-pressure plateau region or the lower plateau region of the inclined plateau

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when the temperature of the said alloy is made higher (T2) during the hydrogen release process, with the result that the amount of effective hydrogen can be increased.

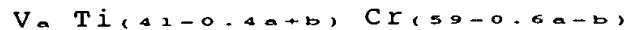
5 It is preferred that the method for absorbing and releasing hydrogen according to the present invention comprises using a hydrogen storage metal alloy wherein the
10 aforementioned adjustment is in such a manner that the composition ratio of the constituent metals for the alloy is adjusted suitably so as to reduce the stability of the
 occluded hydrogen in the alloy within either the low-pressure plateau region or the lower plateau region of the inclined plateau.

15 It is preferred that the method for absorbing and releasing hydrogen according to the present invention comprises using a hydrogen storage metal alloy with a
20 suitably adjusted composition to reduce the stability of the above occluded hydrogen, said hydrogen storage metal alloy being a V alloy containing 0 to 95 at% of at least
 one or more members selected from the group consisting of Nb, Ta, W, Mo, Ti, Cr, Mn, Fe, Al, B, Co, Cu, Ge, Ni and Si.

25 As a result thereof, the alloy having such a composition is highly effective in unstabilizing the occluded hydrogen therein and therefore suitable for
 releasing a great deal of hydrogen from the low-pressure plateau region or the lower plateau region of the inclined plateau by raising the alloy temperature during the hydrogen
30 release process.

 It is preferred that the method for absorbing and releasing hydrogen according to the present invention comprises using a hydrogen storage metal alloy with a
35 suitably adjusted composition to reduce the stability of the above occluded hydrogen, said hydrogen storage metal alloy having a fundamental composition of the formula:

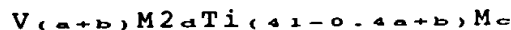
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wherein $0 \leq a \leq 70$ at% and $-10 \leq b \leq 10$ at%.

5 As a result thereof, the alloy having such a composition has not only a great deal of occluded hydrogen therein at the high-pressure plateau region but also a high activity in unstabilizing the hydrogen occluded in the alloy. Therefore, such alloys are suitable for releasing a great
10 deal of hydrogen from the low-pressure plateau region or the lower plateau region of inclined plateau by raising the alloy temperature during the hydrogen release process and highly practicable because a great amount of effective hydrogen is utilizable therein.

15 It is preferred that the method for absorbing and releasing hydrogen according to the present invention comprises using a hydrogen storage metal alloy with a suitably adjusted composition to reduce the stability of
20 the above occluded hydrogen, said hydrogen storage metal alloy having a fundamental composition of the formula:



25 wherein $0 \leq a \leq 70$ at%, $-10 \leq b \leq 10 + c$, $0 \leq c$, $0 \leq d \leq a$, M is at least one or more members selected from the group consisting of Nb, Mo, Ta, W, Mn, Fe, Al, B, C, Co, Cu, Ge, Ln (various lanthanoid metals), N, Ni, P and Si, and M2 is at least one or more members selected from
30 the group consisting of Mo, Nb, Ta, W, Fe and Al.

As a result thereof, the alloy having such a composition has not only a great deal of occluded hydrogen at the high-pressure plateau region but also a high activity in unstabilizing the hydrogen occluded in the alloy.
35 Therefore, such alloys are suitable for releasing a great deal of hydrogen from the low-pressure plateau region or the lower plateau region of inclined plateau by raising the

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alloy temperature during the hydrogen release process and highly practicable because a great amount of effective hydrogen is utilizable therein.

In addition, the suitable admixture with at least one or more elements selected from the group consisting of the above-mentioned lanthanoid metals, N, Ni, P and Si leads to a decrease in the melting point of the alloy and an improvement in the flatness of the plateau resulted thereby whereupon the resultant alloy products are successful in suppressing a decrease in hydrogen adsorption capacity because a heating treatment which is apt to cause a spinodal decomposition is not applied or a treating time is shortened.

It is preferred that the method for absorbing and releasing hydrogen according to the present invention comprises using a hydrogen storage metal alloy wherein the tissue structure of the aforementioned suitably adjusted hydrogen storage metal alloy is of a body-centered cubic structure mono phase without any spinodal decomposition phase or has a body-centered cubic structure together with only a minimum spinodal decomposition phase which is unavoidably produced.

As a result thereof, the hydrogen storage metal alloy has a minimum spinodal decomposition phase or has no spinodal decomposition phase. Therefore, a reduction in the amount of occluded hydrogen by the formation of spinodal decomposition phase can be suppressed as little as possible.

The hydrogen fuel battery of the present invention is characterized in that the battery is equipped with a hydrogen storage tank including a hydrogen storage metal alloy,

a temperature controlling means whereby the above hydrogen storage metal alloy is directly heated or cooled or the atmospheric temperature of the said hydrogen storage metal alloy is raised or cooled,

a fuel battery cell in which hydrogen supplied from

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the said hydrogen storage tank can be subjected to a chemical change to output an electric power, and

a controller where a control is done in such a manner that, with regard to the temperature (T1) of the above hydrogen storage metal alloy during the stage of hydrogen absorption, the temperature of the said alloy during at least one period during the release of hydrogen is made higher (T2) than the temperature (T1) thereof during the above hydrogen-absorbing process.

Such characteristics lead to the following: during the hydrogen release the temperature (T2) of the aforementioned hydrogen storage metal alloy can be made higher than the temperature (T1) during the hydrogen-absorbing process whereby it is now possible to take out as a utilizable hydrogen the occluded hydrogen at the low-pressure plateau region or at the lower plateau region of the inclined plateau, said occluded hydrogen which has been neither desorbed from the hydrogen storage metal alloy nor utilized before, and to increase electric energy obtained by the fuel battery cell.

For the hydrogen fuel battery of the present invention, it is preferred that the aforementioned controller is capable of appropriately controlling a pressure, temperature and flow rate of the hydrogen gas supplied from the above-mentioned hydrogen storage tank to the above-mentioned fuel battery cell.

As a result thereof, the pressure, temperature and flow rate of hydrogen gas can be controlled whereby it is possible to control amounts of generated electric energy in the fuel battery cell appropriately depending upon the load and to enhance the utilizing efficiency of the hydrogen used in the said fuel battery cell.

For the hydrogen fuel battery of the present invention, it is preferred that the above-mentioned temperature controlling means is arranged so as to enable the heat discharged from the above-mentioned fuel battery cell or the exhaust gas discharged from the said fuel battery

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cell to be utilized for the above-mentioned heating.

As a result thereof, the discharged heat or the exhausted heat of the fuel battery cell can be utilized for raising the temperature of the above-mentioned hydrogen storage metal alloy whereby no electric energy or the like is necessary for raising the temperature of such a hydrogen storage metal alloy and the efficiency throughout the hydrogen fuel battery can be enhanced.

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BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a conceptional diagram of a PCT curve
5 of metal V.

FIG. 2 is a graph showing a typical relation between
a hydrogen absorption-dissociation curve and temperature
in LaNi₅, etc.

FIG. 3 is a graph showing amounts of released
10 hydrogen depending on the rise in the temperature upon
hydrogen release in LaNi₅, etc.

FIG. 4 is a graph showing a hydrogen absorption
characteristic (313 K) of V_x-Ti_(40-0.4x)-Cr_(60-0.6x) cast
alloy.

FIG. 5 is a graph showing a hydrogen absorption
15 characteristic under the ordinary cycle in a heat-treated
V_x-Ti_{37.5}-Cr_(62.5-x) alloy.

FIG. 6 is a graph showing an influence of the
measuring temperature on a hydrogen absorption
20 characteristic in a V₇₀Zr_{0.5}Ti_{11.5}Cr₁₈ alloy.

FIG. 7 is a graph showing a hydrogen absorption
and desorption characteristic when the measuring
temperature is 303K and 323K in a V₇₀Zr_{0.5}Ti_{11.5}Cr₁₈ alloy.

FIG. 8 is a graph (conceptional diagram) showing
25 an influence of the temperature difference in a PCT curve
having a two-stage plateau.

FIG. 9 is a graph (conceptional diagram) showing
a volume increase of the temperature difference in a PCT
curve having a two-stage plateau.

FIG. 10 is a graph showing the hydrogen
30 absorption-desorption characteristic obtained by
conducting an ordinary absorption-desorption cycle (the
second cycle) and a cycle according to the method of the
present invention (the third cycle) for a V₄₀Ti₂₅Cr₃₅ alloy.

FIG. 11 is a graph showing a hydrogen
35 absorption-desorption characteristic when the measuring
temperature is 313K in a V₃₀Ti₃₀Cr₄₀ alloy.

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FIG. 12 is a graph showing a hydrogen absorption-desorption characteristic obtained by conducting the fourth and the fifth cycles after the absorption-desorption cycle conducted in FIG. 11.

FIG. 13 is a graph showing a hydrogen absorption characteristic in the third cycle of a $V_{35}Ti_{25}Cr_{40}$ alloy subjected to a heating treatment at 1573K for a given time.

FIG. 14 is a graph showing hydrogen absorption characteristics at 368K of a $V_xTi_{30}Cr_{(70-x)}$ alloy ($x = 27.5, 30, \text{ or } 32.5$).

FIG. 15 is a graph showing a hydrogen absorption characteristic at 313K of a $V_{27.5}Ti_{30}Cr_{42.5}$ alloy.

FIG. 16 is a graph showing an effective hydrogen absorption characteristic when the method of the present invention is applied to a $V_{27.5}Ti_{30}Cr_{42.5}$ alloy.

FIG. 17 is a graph showing a conceptional proof (upon hydrogen release; raised from 313K to 368K, and dissociation pressure controlled) of the differential temperature method using a $V_{20}Ti_{35}Cr_{45}$ sample.

FIG. 18 is a graph showing a hydrogen absorption characteristic when the alloy working method of the present invention is applied to a $V_x-Ti_{(40-0.4x)}-Cr_{(60-0.6x)}$ cast alloy which is an alloy according to the present invention.

FIG. 19 is a hydrogen absorption characteristic graph showing an influence of a temperature rise on dissociation pressure in a $V_{40}Nb_3Ti_{25}Cr_{32}$ alloy.

FIG. 20 is a graph showing a hydrogen absorption characteristic when the differential temperature method of the present invention is applied to a heat-treated $V_x-Ti_{37.5}-Cr_{(62.5-x)}$ alloy.

FIG. 21 is a system flow chart showing an embodiment of the hydrogen fuel battery according to the present invention.

FIG. 22 is a schematic chart showing a mechanism of generation of electric power in the fuel battery cell used in the hydrogen fuel battery of the present invention.

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BEST MODE FOR CARRYING OUT THE INVENTION

As hereunder, the present invention will be
5 illustrated by referring to the drawings.

First, the reason why the composition of the alloy according to the present invention is defined as above is that a reaction of $V \rightarrow VH_{0.5}$ ($\alpha \rightarrow \beta$ phase) in pure V is very stable and it is difficult to dissociate hydrogen from $VH_{0.5}$ under a practical condition but, when it is kept in vacuo at 673K (300 °C) for example, it is possible to dehydrogenate it. In the inventive alloy wherein V is greatly substituted with Ti and Cr, stability of $V(M)H_{0.5}$ ("V(M)" refers to a solid solution of V) is lowered whereby hydrogen is made easily dissociated even at the relatively low practical temperature. Although the alloy of the present invention is in a composition where a spinodal decomposition is apt to take place, it is concluded to be allowed within an extent of being unavoidably formed because, as will be mentioned later in detail, a spinodal decomposition tissue is a source of deterioration of a hydrogen absorption characteristic.

Then the reason for selecting the compositions of the alloy according to the present invention will be explained. Thus, V is capable of forming a BCC mono phase within a composition range of 5 to 100 at%. Further, Ti and Cr are the elements which lower the stability of $VH_{0.8}$ when made into an alloy with V. The atomic radius of Ti (1.47 Å) is bigger than that of V (1.34 Å) and that of Cr (1.30 Å). Therefore, when V is substituted with Ti and Cr and an amount of substituent Ti is more than that of substituent Cr, a lattice constant of the BCC main phase becomes big whereby a plateau pressure of a PCT curve lowers. In the alloy of the present invention, V is greatly substituted with Ti and Cr so as to lessen the stability of $V(M)H_{0.8}$ formed at the above-mentioned lower pressure

plateau is lowered, thereby aiming at increasing an amount of released hydrogen from the said alloy. However, the hydrogen dissociation pressure at the high-pressure plateau region is to be kept within a practical range and, for such a purpose, the substitution ratio of Ti and Cr in the substitution with Ti and Cr as mentioned above comes to an important factor.

The starting composition in the present invention is $V_{70}Ti_{12}Cr_{18}$ (figures are in atomic %). This alloy is a substance derived from pure V by substituting 30 at% of V with 12 at% of Ti and 18 at% of Cr; in other words, wherein 30 at% of V has been replaced therewith at a ratio of Ti:Cr = 4:6. When the total amount of V was replaced therewith at a ratio of Ti:Cr = 4:6, an alloy of $Ti_{40}Cr_{60}$ was produced. In order to suitably adjust pressure conditions, a fundamental composition of the formula:

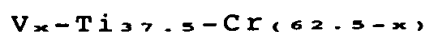


wherein a is an atomic % of V in the alloy, is derived for the composition wherein V is 0 at% in a $Ti_{41}Cr_{59}$ alloy and the range of a falls within $0 \leq a \leq 70$ at%.

FIG. 4 shows a hydrogen absorption characteristic of a $V_x-Ti_{(40-0.4x)}-Cr_{(60-0.6x)}$ cast alloy at 313 K (40°C). It is understood that the alloy wherein the level of V has been made less than 80 at% shows a good characteristic.

In order to allow the dissociation pressure of the alloy to take an appropriate range (in other words, to adjust it depending upon the operating temperature), the term b is set to give an extent for the selection of alloy components so as to enable the dissociation pressure to be adjusted to some extent and $-10 \leq b \leq 10$ at% is basic.

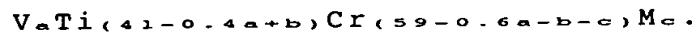
FIG. 5 shows a hydrogen absorption characteristic (the third cycle) at 313K (40°C) of the heat-treated alloy which was produced by subjecting a



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alloy ($x = 0$ to 7.5) to a heating treatment for 1 hour at 1673K (1400°C). It is understood from the drawing that its hydrogen absorption capacity comes to as high as 2.8 mass % when a BCC structure is present by application of a heating treatment even when the level of V in the alloy is as small as 5 to 7.5 atomic %.

Further, in case the Cr component among the alloy components is substituted with other components, when the substituent is M in the alloy and the amount of substituents is c -at%, the basic formula is



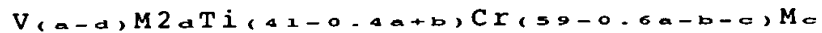
Since there is a tendency that a dissociation pressure increases by a component M, a condition for b is introduced to be $-10 \leq b \leq 10+c$ -at%. This alloy may also be subjected to a hydrogen absorption/desorption at a predetermined temperature like in the conventional case. Although only about one-half of theoretical amount of hydrogen can be taken out in the case of the conventional alloys, there is an advantage in the alloy of the present invention that a great increase in hydrogen desorption capacity is achieved.

As shown in FIG. 5, it is understood that the BCC type V-Ti-Cr system alloy containing a micro amount of V has a high hydrogen storage capacity. It has been known that the element which is apt to form a BCC structure with Ti and Cr, like V, is Mo, Nb, Ta, W, Fe or Al. To aim at a BCC type structure by substituting part of V with such an element is believed to be effective from a phase diagram (the component capable of accelerating the BCC formation will be hereinafter referred to as an M2 term). In case where the V term among the alloy components is replaced with the above M2 term, an amount of the substituent M2 is defined as d -at% ($0 \leq d \leq a$) wherein the M2 component may also be utilized as the above-mentioned substituent term for Cr,

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i.e., the M term.

The hydrogen storage metal alloy according to the present invention provided as such is characterized in that the alloy is a hydrogen storage V type metal alloy having a two-stage plateau characteristic, and has a composition of the following formula:



wherein $0 \leq a \leq 70$ at%, $-10 \leq b \leq 10 + c$, $0 \leq c$, $0 \leq d \leq a$, M is at least one or more elements selected from the group consisting of Nb, Mo, Ta, W, Mn, Fe, Al, B, C, Co, Cu, Ge, Ln (various lanthanoid metals), N, Ni, P and Si, and M2 is at least one or more elements selected from the group consisting of Mo, Nb, Ta, W, Mn, Fe and Al, and the main phase of the alloy is in a body-centered cubic structure and do not have a spinodal decomposition tissue or has a spinodal decomposition phase which is unavoidably produced.

The method of the present invention is a method for effectively utilizing the occluded hydrogen in a low-pressure plateau region of hydrogen storage metal alloy showing a two-stage plateau or inclined plateau characteristic which comprises:

absorbing hydrogen at a low temperature region (T1),

elevating a temperature during a hydrogen release process, and

increasing a hydrogen dissociation pressure of the low-pressure plateau region at an elevated temperature region (T2 > T1) whereby the hydrogen at the low-pressure plateau region is released.

The lowest limit in the above low-temperature region (T1) is an extremely low temperature in a living area

where hydrogen can be utilized as an energy source and, at present, 243K is an example of such an extremely low temperature. The above elevated temperature region (T2) is a temperature which is higher than the above
5 low-temperature region (T1) which is the hydrogen-absorbing temperature. The above elevated temperature region (T2) can be achieved by the use of a waste heat (usually about 70 to 100°C) generated at the fuel battery member upon operation (i.e., corresponding to the hydrogen
10 release process) or a heat from a heater exclusively therefor when the hydrogen storage metal alloy is used, for example, as a tank for a fuel battery.

Although the method for absorbing and releasing hydrogen according to the present invention is applicable
15 to various kinds of a body-centered cubic type hydrogen storage metal alloy, it is preferably applicable to V alloys, particularly, to hydrogen storage V metal alloys containing each 0 to 95 at% of at least one or more elements selected from the group consisting of Ti, Cr, Nb, Mo, Ta, W, Mn, Fe,
20 Al, B, C, Co, Cu, Ge, Ln (various lanthanoid metals), N, Ni, P and Si.

More preferably, when a method for absorbing and releasing hydrogen which comprises
absorbing hydrogen with an alloy wherein the
25 stability of $VH_{0.5}$ (or $V(M)H_{0.5}$, i.e., a low-pressure plateau region) is lowered, and releasing hydrogen at an elevated temperature on
a
30 final hydrogen release stage,
is applied, it is possible to absorb and desorb a much greater deal of hydrogen. With regard to a hydrogen release cycle, the desorption may be carried out at the temperature which is same as that at hydrogen-absorption (the low temperature
35 which has been mentioned until now; T1) during a part of the period but, at least in the final stage of desorption, it is necessary to adjust to the above-mentioned high

temperature (T2) by means of heating so that hydrogen is sufficiently desorbed. Preferably, hydrogen at the above high-pressure plateau part is desorbed at a relatively low temperature (which may be the same temperature as the above-mentioned T1) and, for taking out the hydrogen from the above-mentioned low-temperature plateau part at the final stage of the desorption of hydrogen, the alloy is heated to make the temperature high as mentioned above (T2) and to desorb the hydrogen.

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As hereunder, the inventive effects of the method for absorbing and releasing hydrogen according to the present invention will be more specifically illustrated by citing the experiments conducted by the present inventors. Unless otherwise mentioned, the alloys used as samples were prepared in such a manner that the materials were weighed so as to bring the weight of ingot to 14 g, arc-melted in an argon atmosphere of 40 kPa and dissolved and stirred repeatedly three times for enhancing the uniformity and the resulting cast ingots per se were used as samples or subjected to a heating treatment for homogenization at 1473K for 2 hours in an Ar atmosphere.

First, a measurement was carried out for $V_{70}Zr_{0.5}Ti_{11.5}Cr_{18}$ alloys wherein an large amount of V was contained, which have been briskly studied at present. Before the measurement, a full deaeration was carried out at the measuring temperature and then hydrogen absorption characteristics were examined at a given measuring temperature. The results are shown in FIG. 6 (pressure vs composition isothermal curve: PCT line chart). It is understood from FIG. 6 that the lower the measuring temperature, the lower the plateau pressure and the more the hydrogen storage amount.

The results of the measurement at 303K (30°C) and 323K (50 °C) for hydrogen absorption and desorption characteristics of the above $V_{70}Zr_{0.5}Ti_{11.5}Cr_{18}$ alloy are

shown in FIG. 7. When the hydrogen release characteristics at 303K and 323K are compared, it is noted that a greater amount of hydrogen can be released when the operation is carried out at the elevated temperature of 323K. When the results of FIG. 6 and FIG. 7 are summarized together, it has been noted that a much greater amount of hydrogen can be absorbed and released if hydrogen is absorbed at low temperature and hydrogen is desorbed at high temperature. Unlike the conventional hydrogen storage metal alloy having a one-stage plateau (refer to FIG. 2), the hydrogen storage metal alloy having a two-stage plateau region does not show a clear decrease in amounts of absorbed and desorbed hydrogen even when operated at high temperature because the low-pressure plateau region or the inclined plateau region contributes to absorption and desorption of hydrogen when operation is carried out at high temperature as noted from the results as shown in FIG. 7, i.e., the hydrogen storage metal alloy begins to utilize a low-pressure plateau region.

When the PCT curves (FIG. 2 and FIG. 3) of the hydrogen storage metal alloy having a one-stage plateau mentioned in the paragraphs of Related Art of the Invention are checked once again, an increase in a hydrogen release curve by making the temperature high rarely occurs in the case of a one-stage plateau alloy. Therefore, it is understood that elevation of the operation temperature in the hydrogen release process is quite effective for an increase in the amount of released hydrogen with regard to the hydrogen storage metal alloy having a two-stage plateau or an inclined plateau region.

Now, based upon the experimental results of FIG. 6 and FIG. 7 and by referring to the PCT curve (conceptual chart) of V metal shown in FIG. 1, a conceptual chart depicting an influence of the temperature difference in the PCT curve having a two-stage plateau has been prepared and

is shown as FIG. 8. An increase in the amount of desorbed hydrogen is noted in the $V_{70}Zr_{0.5}Ti_{11.5}Cr_{18}$ alloy which has been examined. Then, a comparison has been made for the cases when operations were carried out at a low temperature T1 and a high temperature T2. Although there is nearly no difference in the amounts of absorbed and desorbed hydrogen between the two, it is likely that there occurs a big difference in the amounts of the residual hydrogen in the alloy. Now, when hydrogen was absorbed at low temperature T1 and released at higher temperature T2 than T1 (in other words, a differential temperature method was applied), a conceptional chart is shown in FIG. 9 which shows an increase in the hydrogen capacity. Unlike the conventional hydrogen storage metal alloy having a single plateau region, it is understood from FIG. 9 that it is possible to increase the amounts of absorbed and released hydrogen in the case of a hydrogen storage metal alloy having a two-stage plateau when such an alloy can be suitably designed and adjusted and a temperature may be elevated mostly at the taking stage of hydrogen release process so as to lead to an increase in the operation temperature with regard to the hydrogen storage metal alloy having an inclined plateau whereby a site related to a low-pressure plateau can be contributed to the hydrogen absorption/release. According to a principle which is different from the hydrogen storage metal alloy having a one-stage plateau alloy, the present inventors have found a possibility that an increase in amounts of released hydrogen can be achieved or a high capacity can be acquired for hydrogen storage metal alloy-equipped hydrogen tanks.

However, it has been well known as already mentioned in the above the paragraphs of Related Art of the Invention that it is impossible to increase an amount of released hydrogen (i.e., to take out a sufficient amount of hydrogen from the low-pressure plateau region) by heating up to about 100°C. An increase in the hydrogen storage

amount by a differential temperature method has not been investigated yet. Thus, it can be concluded that the $V_{70}Zr_{0.5}Ti_{11.5}Cr_{18}$ alloy of the present invention is capable of achieving an increase in the hydrogen release amount with elevating the temperature during the desorption stage, relying on a new principle different from the conventional V alloy. The fact that such a conclusion can be applied to known V alloys having different compositions has been confirmed as follows:

The $V_{40}Ti_{25}Cr_{35}$ alloy which was reported in the aforementioned JP, A, 10-110225 (having a spinodal decomposition tissue as a result of a heat-treatment at 1473K for 2 hours) was subjected to an activating treatment followed by measurement for the first cycle and the second cycle at 313K (40°C), and further subjected to a deaeration at room temperature for 5 hours or more, and then at 368K (95°C) for 3 hours followed by measurement for the third cycle at 313K. The PCT curves at the second cycle and the third cycle are shown in FIG. 9. In the second cycle wherein a usual hydrogen absorption/desorption process was carried out, the amount of hydrogen which could be reversibly taken out therefrom was about 2.4 mass % which was in the same degree as that in the conventional report while in the third cycle wherein an elevated temperature process was introduced into the second cycle which was at the same low temperature as in the conventional case the amount of occluded hydrogen slightly increased to 2.49 mass %.

Based upon these results, it is difficult to increase an amount of stored hydrogen by a hydrogen desorption reaction from $V(M)H_{0.8}$ with regard to a BCC type alloy containing about 40 at% of V. However, when a high-temperature cycle is carried out after the low-temperature cycle, the amount of occluded hydrogen increases. The efficacy of the alloy operation method per se according to the present invention has been confirmed. Therefore, it is concluded that the amount of occluded hydrogen will increase if an improvement is carried out for

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the composition.

5 A $V_{30}Cr_{30}Ti_{40}$ alloy (having a spinodal decomposition tissue similarly to the alloy of FIG. 6) wherein the amount of V was further reduced as an alloy with an optimum composition to which the above cycle for effectively utilizing hydrogen was applicable was measured for PCT curve up to 3 cycles at the constant temperature of 313K. The results are shown in FIG. 1. The hydrogen storage amount obtained as a result thereof is in a similar degree with one reported already.

10 Next, in order to confirm the effectiveness of the method according to the present invention, a PCT curve measured at 313K after deaeration at 368K for 2 hours as the fourth cycle and a PCT curve measured after deaeration at 363K for 5 hours as the fifth cycle are shown in FIG. 12. It is confirmed that the amount of occluded hydrogen increases from 2.45 mass % to 2.8 mass % when the method of the present invention is applied. The important thing here is that an increase in the amount of occluded hydrogen is observed and the hydrogen absorption capacity amounts up to about 2.8 mass % for the $V_{30}Cr_{30}Ti_{40}$ alloy in spite of the fact that the $V_{30}Cr_{30}Ti_{40}$ alloy is not deaerated at room temperature and the desorption time is shorter than in the case of the aforementioned $V_{40}Ti_{25}Cr_{35}$ alloy (being deaerated at room temperature before deaeration at high temperature). Therefore, according to the method of the present invention for absorbing and releasing hydrogen, it is possible to take out the hydrogen more efficiently from the low-pressure region as compared with the conventional operation at the constant temperature whereby it is noted that an effectively utilizable amount of occluded hydrogen can be significantly increased.

35 FIG. 13 shows a PCT absorption curve each of as cast and as heat-treated at 1573K for various retention time ranges $V_{35}Ti_{25}Cr_{40}$ alloys. The results show that the hydrogen-absorption characteristic is better in the case

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where a heating treatment is not carried out at all or where the time for a heating treatment is as short as possible than the alloy which is fully in the form of a spinodal decomposition. Based upon such a finding, it is decided to permit the tissue of the alloys according to the present invention so far as it is in a BCC mono phase without any spinodal decomposition phase or with only a spinodal decomposition phase unavoidably produced. The phrase "unavoidably produced" as used herein refers to shorter than 2 minutes which is slightly longer than -●- in FIG. 13 and, when the time is as short as such, the alloy may be kept within a spinodal decomposition range. In the meanwhile, it will be apparent from the above illustration that, when the method of the present invention is applied to the alloy where the heating time is 2 to 50 hours in FIG. 13, the corresponding increase in the hydrogen storage amount can be achieved.

It will be also apparent that, since the low-temperature plateau region of the hydrogen storage metal alloy showing the two-stage plateau as mentioned above can be effectively utilized, the method of the present invention is applied to an alloy showing an inclined plateau whereby the low-temperature region can be effectively utilized for hydrogen absorption.

Then, a PCT curve measured at 368K for a $V_xTi_{3.0}Cr_{(7.0-x)}$ alloy wherein the amount of V was varied is shown in FIG. 14. From the results of FIG. 14, it is noted that, at this temperature, hydrogen absorption took place up to 2.65 mass % and all of the occluded hydrogen, especially in the case of a $V_{27.5}Ti_{3.0}Cr_{42.5}$ alloy, was desorbed. In the conventional alloy, only about one-half of the theoretical amount of hydrogen can be taken out; however, when hydrogen is taken out at 368K, the conclusion is that all of the occluded hydrogen in the sample can be effectively utilized.

The results when the method of the present invention was applied to this sample are shown in FIG. 15. Thus, the first cycle was carried out at the constant temperature in the same manner as in the conventional case, then a deaeration was carried out at 368K in each of the second and third cycles before measurement and the measurement was carried out at 313K whereupon the amount of occluded hydrogen increased up to 2.8 mass %. Accordingly, when hydrogen is absorbed with a $V_{27.5}Ti_{30}Cr_{42.5}$ alloy at 313K and desorbed at 368K, the hydrogen can be utilized to the maximum extent. The results are shown in FIG. 16. The effectively utilized hydrogen amount is the difference between the hydrogen storage amount at 7 Mpa in the hydrogen-absorbing process at 313K and the residual hydrogen amount in the alloy at 0.01 MPa in the hydrogen release process at 368K. Accordingly, it is 2.7 mass %.

Similarly, the results of the present invention applied to a melt-prepared $V_{20}Ti_{35}Cr_{45}$ alloy are shown in FIG. 17.

In the drawing, there are shown PCT curves in the hydrogen release process for (1) the case (Δ) where hydrogen absorption and desorption was carried out at 368K (90°C), (2) a cycle (\square) wherein a differential temperature method was introduced in such a manner that hydrogen desorption was carried out at 368K and thereafter hydrogen absorption and desorption was carried out at 313K (40°C), and (3) a cycle (\bullet) where hydrogen desorption was carried out at 368K, hydrogen absorption was carried out at 313K and, during the hydrogen release process, heating was carried out up to 368K with monitoring the dissociation pressure after hydrogen desorbing to an equilibrium hydrogen dissociation pressure of 0.05 MPa.

The curve shown by \square is the case where hydrogen desorption was carried out at 368K and then hydrogen absorption was carried out at 313K showing a big storage amount. Accordingly, it is noted that the differential

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temperature method is effective.

The curve shown by ● is the case where the operating temperature was elevated when the equilibrium dissociation pressure during the hydrogen release process arrived 0.05 MPa (temperature for each stage is mentioned in the drawing) and, as a result of heating, the dissociation pressure was controlled, the plateau region was flattened and the effective amount of hydrogen was greatly increased. It is noted from the drawing that the residual hydrogen amount in the alloy at 0.005 MPa is identical with that in the desorption curve (Δ) obtained at 368K.

Thus, it is noted that, when a differential temperature method is used, the amount of occluded hydrogen increases and, if the temperature is elevated during the hydrogen desorption, the effectively utilizable hydrogen amount increases.

Then, the results when the alloy operating method of the present invention, i.e., the differential temperature method, was applied to a $V_x-Ti_{(40-0.4x)}-Cr_{(60-0.6x)}$ cast alloy are shown in FIG. 18. As shown herein the alloy wherein the level of V is brought to from 20 to 60 at% exerts the hydrogen storage capacity of about 2.85 to 2.95 mass %. When this is compared with FIG. 4, it is noted that, when the method of the present invention is applied, an increase in a hydrogen capacity to an extent of about 0.2 to 0.3 mass % is confirmed whereby the effectiveness and usefulness of the present invention are noted.

Further, as mentioned already, when a $V_{40}Ti_{25}Cr_{35}$ alloy which was reported to occlude about 2.4 mass % of hydrogen was subjected to an absorption/desorption treatment by the present invention, a hydrogen storage amount increased up to 2.49 mass %. The results where it was partially substituted with Nb having a strong tendency of forming a BCC solid solution are also shown in FIG. 15 while PCT curves of a $V_{40}Ti_{25}Cr_{35}Nb_5$ alloy as measured at the third and the fourth cycles and at 368K are shown in

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FIG. 19. From the results, it is believed that hydrogen storage amounts increased by substitution with Nb and a dissociation pressure of the low-pressure plateau region increased when the temperature was raised to 368K. The effectively utilizable hydrogen amount is 2.7 mass %. It is noted that, as such, the hydrogen storage amount increases and the utilizable effective hydrogen amount increases by the method of the present invention even in the known alloys by substituting with Nb.

FIG. 20 shows the results when the differential temperature method of the present invention was applied to a heat-treated $V_x-Ti_{37.5}-Cr_{(62.5-x)}$ alloy exerting the hydrogen storage amount of as high as 2.8 mass % (refer to FIG. 5). Even in the alloys where the level of V is brought to as small as 5 to 7.5 atom %, a hydrogen storage amount of about 3.0 mass % is achieved when the present invention is applied. When a comparison is made with the results of FIG. 5 (absorption/desorption at the single temperature of 313K in the same fashion as in the conventional method), an increase of about 0.2 mass % in the hydrogen capacity is noted upon application of the present invention whereby the effectiveness and usefulness of the present invention are noted. Especially in the case which is shown hereinabove, only the results are shown within such a temperature range where the utilization of waste heat is easy but it is also possible to form a high capacity hydrogen storage metal alloy tank in a different manner when a heating apparatus is installed in the hydrogen storage metal alloy tank either auxiliary or positively and a heating is carried out at the final stage of the hydrogen release process.

As an example of the present invention, there is shown a case where hydrogen was occluded at 313K (40°C) and desorbed at 368K (95°C). When the hydrogen-absorbing process is carried out at lower temperature and the hydrogen desorption process is carried out at higher temperature, however, the effective amount of utilizable hydrogen further increases.

FIG. 21 is a system flow chart showing a preferred
embodiment of the hydrogen fuel battery according to the
present invention. FIG. 22 is a schematic chart showing
a mechanism of generation of electric power in the fuel
battery cell used in the hydrogen fuel battery of the present
invention.

a hydrogen fuel tank (4) installed with a hydrogen storage metal alloy in which the composition of constituent elements is suitably adjusted so as to make the occluded hydrogen desorbable in the low-pressure plateau region by means of heating according to the present invention, said fuel tank (4) being capable of supplying the hydrogen occluded in the said hydrogen storage metal alloy to a fuel battery cell

the said fuel battery cell (1) in which hydrogen supplied from the said hydrogen fuel tank (4) is used as a fuel and the said hydrogen is made to react with oxygen to change to water whereby the electric power can be taken out while water is decomposed upon application of electric power on the contrary whereby the hydrogen can be supplied

an inverter (2) in which a direct current electric power output from the said fuel battery cell (1) is converted to a predetermined alternating current electric power;

a controller (3) for conducting various control for elevating or lowering the temperature of the hydrogen storage metal alloy in the said hydrogen fuel tank (4), mass control for pressure, flow rate, temperature, etc. with regard to hydrogen supplied to the said fuel battery cell (1) and control for each of the above-mentioned members.

As hereunder, the operation of the hydrogen fuel battery according to the present embodiment will be illustrated. At first, a step of hydrogen absorption with the hydrogen storage metal alloy in the above-mentioned hydrogen fuel tank (4) will be illustrated.

Firstly, the hydrogen which is to be absorbed with the hydrogen storage metal alloy is supplied, as a starting material hydrogen (shown in FIG. 21), into the hydrogen fuel tank (4) by connecting a high-pressure hydrogen cylinder 35 to a hydrogen supplying outlet followed by opening the valve (V1) whereupon the hydrogen storage metal alloy absorbs the

Simultaneously, the above-mentioned controller (3) releases the valves (V9 and V10) connected to the heat exchanger (5) and also makes the pump (P5) in an operating state whereby the outer air is sent into the heat exchanger (5) to cool the above-mentioned cold/warm water with the outer air. At the same time, the hydrogen storage metal alloy is monitored for the temperature with the above-mentioned temperature sensor (TS3) and the circulation pump (P3) is appropriately operated so as to bring the temperature (T1) of the said hydrogen storage metal alloy to 40°C or lower whereby the above heat-exchanged cold/warm water is appropriately passed into the above-mentioned cooling/warming medium jacket to carry out the cooling of the hydrogen storage metal alloy. When the predetermined amount of hydrogen is absorbed, the above-mentioned valve (V11) is closed and hydrogen absorption is finished.

Each operation of the members including the

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As a result of heating as such, the temperature of the above-mentioned hydrogen storage metal alloy is elevated and as aforementioned the occluded hydrogen in the lower region of the inclined plateau or in the low-pressure plateau region is desorbed. Such a desorbed hydrogen is supplied to the fuel battery cell (1) so that generation of electric power is continuously carried out whereupon the electric power generating capacity of the hydrogen fuel battery can be significantly improved.

With regard to the heating temperature (T2) of such a hydrogen storage metal alloy, since water is used as a cooling/warming medium in this example, its upper limit is around 90°C but the present invention is not limited to. Such a hydrogen storage metal alloy may be heated with a heater or the like to bring it to a higher temperature. Further, in this example, temperature upon hydrogen absorption is made not higher than 40°C which is practical by means of cooling due to heat release with a heat exchange

to the outer air but the present invention is not limited to. Such a cooling may be carried out by installment of a cooling apparatus or by using as the cooling/warming medium a cooling medium such as flon or ammonia together with a heat pump in which a heat exchange is carried out by compression and expansion of such a cooling medium. Furthermore, in place of such a heat pump, it is also possible to carry out both cooling and heating by the use of a Peltier element.

It is preferred to use a heat exchanger (5) as mentioned above since much electric power is not necessary for heating and cooling, the resulting electric power from the said hydrogen fuel battery can be increased greatly and the efficiency of the hydrogen fuel battery can be improved although the present invention is not limited thereto.

At a next step, when release of hydrogen as such is finished and fresh hydrogen is to be stored, there is a method, in addition to the means of supplying the starting material hydrogen to the hydrogen fuel tank (4) as mentioned above, where electric power is applied to the above-mentioned fuel battery cell (1) and hydrogen produced by decomposition of water is stored.

The above means will be illustrated as follows:

At first, a predetermined direct current is applied to the above-mentioned fuel battery cell (1),

the pump (P4) is operated under the condition where the valve (V4) is closed,

an outer air is passed into the water which is stored in the storage tank via the above-mentioned generation of electric power so as to contain steam and

the air containing the said steam is supplied into the fuel battery cell (1) via the valve (V6).

As a result, water is adhered onto the surface of the positive electrode side in the said fuel battery cell (1), the said adhered water is electrolyzed to give oxygen, air containing the said oxygen is discharged outside the fuel battery cell (1) while hydrogen produced

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